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(54) Titre : COMBINAISON SYNERGISTE IGNIFUGEANTE POUR POLYMERES
(54) Title: SYNERGISTIC FLAMEPROOFING COMBINATION FOR POLYMERS

(57) Abrégé/Abstract:
The present invention relates to a synergistic flameproofing combination for polymers, in particular for ABS, which contains, as component A, a phosphinic acid salt of the formulae (I) defined in the description and/or a diphosphinic acid salt of the formula (II) and/or polymers thereof and which contains, as component B, a nitrogen-containing phosphate or a mixture of the compounds defined by the formulae.

1997DE108

Clariant GmbH

Abstract

Synergistic flameproofing combination for polymers

The present invention relates to a synergistic flameproofing combination for polymers, in particular for ABS, which contains, as component A, a phosphinic acid salt of the formulae (I) defined in the description and/or a diphosphinic acid salt of the formula (II) and/or polymers thereof and which contains, as component B, a nitrogen-containing phosphate or a mixture of the compounds defined by the formulae.

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Description

The invention relates to a synergistic flameproofing combination which contains calcium, aluminum or zinc phosphinates and nitrogen-containing phosphates.

Polymers are frequently rendered flame-retardant by adding to them phosphorus-containing or halogen-containing compounds or mixtures thereof. Mixtures of phosphorus- and nitrogen-containing compounds are also often used as flame retardants.

Alkali metal salts of phosphinic acid have already been proposed as flame-retardant additives for polyesters (DE-A-2 252 258). They must be introduced in amounts of up to 30% by weight and some of them have a disadvantageous, corrosion-promoting effect on the processing machines.

Furthermore, the salts of phosphinic acids with an alkali metal or with a metal from the second or third main group or subgroup of the Periodic Table have been used for the preparation of flame-retardant polyamide molding materials, in particular the zinc salts (DE-A-2 447 727).

Calcium and aluminum phosphinates have proven particularly effective in polyesters (EP-A-699 708). However, the preparation of these phosphinates on an industrial scaleis relatively complicated and expensive, which very greatly limits the potential uses of the products as flame retardants for plastics.

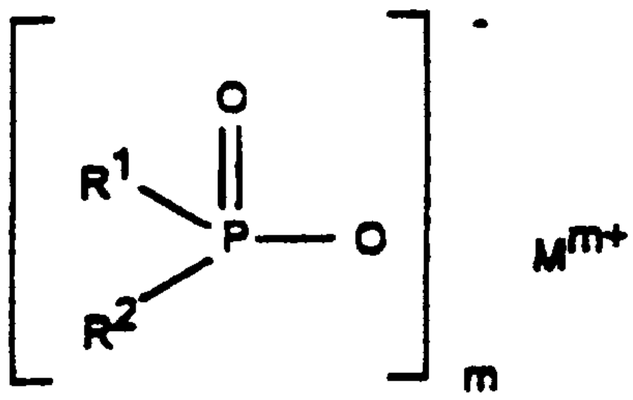
The application PCT/EP97/01644 (WO97/39053) describes synergistic combinations of different phosphinates

with heat-stable organic nitrogen compounds which are not very volatile and have a particularly good and also economical flameproofing effect in polymers.

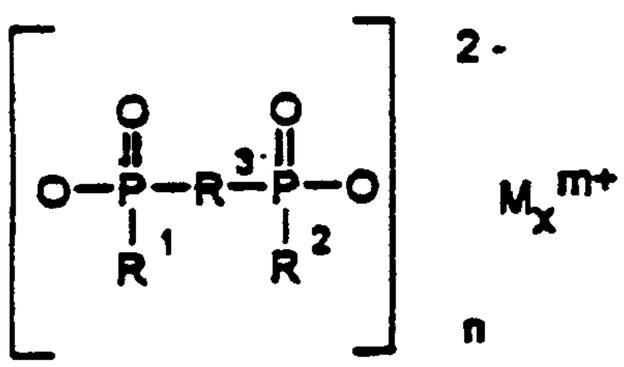
Aluminum hydroxide or phosphate, too, can be used in mixtures with said phosphinic acid salts as a flame-retardant additive, even if the synergistic action is not so pronounced as in the case of the organic nitrogen compounds.

It was found, surprisingly, that nitrogen-containing, purely inorganic phosphates mixed with the phosphinates have an action which is similarly good but in some cases even better. In addition, compared with commercial flame-retardant molding materials, molding materials treated according to the invention have high light stability if light stabilizers of the type comprising sterically hindered amines and/or UV absorbers are used together with the flameproofing mixtures.

The invention thus relates to a synergistic flameproofing combination for polymers which contains, as component A, a phosphinic acid salt of the formula (I) and/or a diphosphinic acid salt of the formula (II) and/or polymers thereof



(I)



(II)

in which

R^1 and R^2 are linear or branched C_1-C_6-alkyl, preferably C_1-C_4-alkyl, e.g. methyl, ethyl, n-propyl, isopropyl, n-butyl, tert-butyl or n-pentyl, or phenyl;

R^3 is linear or branched C_1-C_{10}-alkylene, preferably C_1-C_6-alkylene, e.g. methylene, ethylene, n-propylene, isopropylene, n-butylene, tert-butylene, n-pentylene, n-octylene or n-dodecylene;

C_6-C_{10}-arylene, e.g. phenylene or naphthylene, preferably phenylene;

alkylarylene, e.g. methylphenylene, ethylphenylene, tert-butylphenylene, methylnaphthylene, ethylnaphthylene or tert-butylnaphthylene; or

arylalkylene, e.g. phenylmethylene, phenylethylene, phenylpropylene or phenylbutylene;

M is a calcium, aluminum or zinc ion, preferably an aluminum ion;

m is 2 or 3;

n is 1 or 3;

x is 1 or 2,

and which contains, as component B, a nitrogen-containing phosphate of the formulae $(NH_4)_yH_{3-y}PO_4$ or $(NH_4PO_3)_z$, in which y may assume numerical values from 1 to 3 and z is any desired number, typically also the average value of a chain length distribution.

In one aspect, this invention provides the use of a flameproofing combination, as described, for flameproofing polymers.

In another aspect, this invention provides a flameproofed plastics molding material, containing a flameproofing combination as described above.

Below, the term "phosphinic acid salt" denotes salts of phosphinic and diphosphinic acids and polymers thereof.

The phosphinic acid salts, which are prepared in aqueous medium, are essentially monomeric compounds.

Depending on the reaction conditions, polymeric phosphinic acid salts can also form under certain circumstances.

Suitable phosphinic acids as a component of the phosphinic acid salts are, for example:

dimethylphosphinic acid, ethylmethylphosphinic acid, diethylphosphinic acid, methyl-n-propylenephosphinic acid, methanedi(methylphosphinic acid), benzene-1,4-(dimethylphosphinic acid), methylphenylphosphinic acid and diphenylphosphinic acid.

The salts of the phosphinic acids according to the invention can be prepared by known methods which are described in more detail in EP-A-699 708. The phosphinic acids are reacted in aqueous solution with metal carbonates, metal hydroxides or metal oxides.

Polymers in the context of the invention are also described on pages 6 to 9 of the application PCT/EP97/01664, as given below:

1. Polymers of mono- and diolefins, for example polypropylene, polyisobutylene, polybutylene, poly-1-butene, polyisoprene or polybutadiene and also polymers of cycloolefins such as, for example, of cyclopentene or norbornene; and also polyethylene (which may be crosslinked); for example high-density polyethylene (HDPE), polyethylene of high density and high molar mass (HDPE-HMW), polyethylene of high density and ultra high molar mass (HDPE-UHMW), medium-density polyethylene (MDPE), low-density polyethylene (LDPE), linear low density polyethylene (LLDPE), branched low-density

polyethylene (BLDPE).

2. Mixtures of the polymers set out under 1), for example mixtures of polypropylene with polyisobutylene, polypropylene with polyethylene (e.g. LDPE/HDPE, PP/LDPE) and mixtures of different types of polyethylene (e.g. LDPE/HDPE).

3. Copolymers of monoolefins and diolefins with one another or with other vinyl monomers, for example ethylene-propylene copolymers, linear low-density polyethylene (LLDPE) and mixtures thereof with low-density polyethylene (LDPE), propylene-1-butene copolymers, propylene-isobutylene copolymers, ethylene-1-butene copolymers, etc. Additionally, ethylene-alkyl acrylate copolymers, ethylene-vinyl acetate copolymers and copolymers thereof with carbon monoxide, or ethylene-acrylic acid copolymers and salts thereof (ionomers), and also terpolymers of ethylene with propylene and a diene, such as hexadiene, dicyclopentadiene or ethylidenenorbornene; and also mixtures of such copolymers with one another and with polymers set out under 1), for example polypropylene/ethylene-propylene copolymers, LDPE/ethylene-vinyl acetate copolymers, LDPE/ethylene-acrylic acid copolymers, LLDPE/ethylene-vinyl acetate copolymers, LLDPE/ethylene-acrylic acid copolymers and alternating or random polyalkylene-carbon monoxide copolymers and mixtures thereof with other polymers such as, for example, polyamides.

4. Polystyrene, poly(p-methylstyrene), poly-(α-methylstyrene).

5. Copolymers of styrene or α-methylstyrene with dienes or

acrylic derivatives, for example styrene-butadiene, styrene-acrylonitrile, styrene-alkyl methacrylate, styrene-butadiene alkyl acrylate and methacrylate, styrene-maleic anhydride, styrene-acrylonitrile-methacrylate; mixtures of high impact strength comprising styrene copolymers and another polymer, for example a polyacrylate, a diene polymer or an ethylene-propylene-diene terpolymer; and block copolymers of styrene, for example styrene-butadiene-styrene, styrene-isoprene-styrene, styrene-ethylene/butylene-styrene or styrene-ethylene/propylene-styrene.

6. Graft copolymers of styrene or α-methylstyrene, for example styrene on polybutadiene, styrene on polybutadiene-styrene or polybutadiene-acrylonitrile copolymers, styrene and acrylonitrile (and/or methacrylonitrile) on polybutadiene; styrene, acrylonitrile and methyl methacrylate on polybutadiene; styrene and maleic anhydride on polybutadiene; styrene, acrylonitrile and maleic anhydride or maleimide on polybutadiene; styrene and maleimide on polybutadiene; styrene and alkyl acrylates and/or alkyl methacrylates on polybutadiene, styrene and acrylonitrile on ethylene-propylene-diene terpolymers, styrene and acrylonitrile on polyalkyl acrylates or polyalkyl methacrylates, styrene and acrylonitrile on acrylate-butadiene copolymers, and mixtures thereof with the copolymers set out under 5), as are known, for example, as ABS, MBS, ASA or AES polymers.

7. Halogen-containing polymers, for example polychloroprene, chlorinated rubber, chlorinated and brominated isobutylene-

isoprene copolymer (halobutyl rubber), chlorinated or chlorosulfonated polyethylene, copolymers of ethylene and chlorinated ethylene, epichlorohydrin homo- and copolymers, especially polymers of halogen-containing vinyl compounds, for example polyvinyl chloride, polyvinylidene chloride, polyvinyl fluoride, polyvinylidene fluoride; and also copolymers thereof, such as vinyl chloride-vinylidene chloride, vinyl chloride-vinyl acetate or vinylidene chloride-vinyl acetate.

8. Polymers derived from α,β-unsaturated acids and their derivatives, such as polyacrylates and polymethacrylates, and impact-modified (using butyl acrylate) polymethyl methacrylates, polyacrylamides and polyacrylonitriles.

9. Copolymers of the monomers set out under 8) with one another or with other unsaturated monomers, for example acrylonitrile-butadiene copolymers, acrylonitrile-alkyl acrylate copolymers, acrylonitrile-alkoxyalkyl acrylate copolymers, acrylonitrile-vinyl halide copolymers or acrylonitrile-alkyl methacrylate-butadiene terpolymers.

10. Polymers derived from unsaturated alcohols and amines and/or their acyl derivatives or acetals, such as polyvinyl alcohol, polyvinyl acetate, stearate, benzoate and maleate, polyvinylbutyral, polyallyl phthalate, polyallylmelamine; and copolymers thereof with olefins mentioned in section 1.

11. Polyacetals, such as polyoxymethylene, and those polyoxymethylenes comprising comonomers such as, for example, ethylene oxide; polyacetals which are modified with thermoplastic polyurethanes, acrylates or MBS.

12. Polyphenylene oxides and sulfides and mixtures thereof with styrene polymers or polyamides.

13. Polyamides and copolyamides derived from diamines and dicarboxylic acids and/or amino carboxylic acids or the corresponding lactams, such as polyamide 4, polyamide 6, polyamide 6/6, 6/10, 6/9, 6/12, 4/6, 12/12, polyamide 11, polyamide 12, aromatic polyamides prepared starting from m-xylene, diamine and adipic acid; polyamides prepared from hexamethylenediamine and from iso- and/or terephthalic acid, with or without an elastomer as modifier, for example poly-2,4,4-trimethyl-hexamethyleneterephthalamide or poly-m-phenyleneisophthalamide; block copolymers of the abovementioned polyamides with polyolefins, olefin copolymers, ionomers, or chemically bonded or grafted elastomers; or with polyethers, for example with polyethylene glycol, polypropylene glycol or polytetramethylene glycol. Additionally, copolyamides or polyamides modified with EPDM or ABS; and polyamides which are condensed in the course of processing (RIM polyamide systems).

14. Polyureas, polyimides, polyamideimides, polyetherimides, polyesterimides, polyhydantoins and polybenzimidazoles.

15. Polyesters derived from dicarboxylic acids and dialcohols and/or from hydroxycarboxylic acids or the corresponding lactones, such as polyethylene terephthalate, polybutylene terephthalate, poly-1,4-dimethylolcyclohexane terephthalate, polyhydroxybenzoates, and also block polyether esters derived from polyethers having hydroxyl end groups; additionally,

polyesters modified with polycarbonates or MBS.

16. Polycarbonates and polyester carbonates.

17. Polysulfones, polyether sulfones and polyether ketones.

18. Mixtures (polyblends) of the abovementioned polymers, for example PP/EPDM, polyamide/EPDM or ABS, PVC/EVA, PVC/ABS, PVC/MBS, PC/ABS, PBTP/ABS, PC/ASA, PC/PBT, PVC/CPE, PVC/acrylates, POM/thermoplastic PU, PC/thermoplastic PU, POM/acrylate, POM/MBS, PPO/HIPS, PPO/PA 6.6 and copolymers.

The amount of the phosphinic acid salt of the general formula I which is to be added to the polymers, or of the diphosphinic acid salt of the formula II, may vary within wide limits. In general, from 1 to 30% by weight, based on the prepared polymer compound, are used. The optimum amount depends on the nature of the polymer, on the type of component B and on the type of the phosphinic acid salt itself which is used and can be readily determined by experiments. From 3 to 20, in particular from 5 to 15, % by weight are preferred.

The phosphinic acid salts according to the invention can be used in different physical forms, depending on the polymer used and on the desired properties. Thus, the phosphinic acid salts may be milled to give a finely divided form, for example for achieving better dispersion in the polymer. If desired, mixtures of different phosphinic acid salts may also be used.

The phosphinic acid salts according to the invention are thermally stable and neither decompose the polymers during processing nor influence the preparation process of the plastics molding material. The phosphinic acid salts are nonvolatile under preparation and processing conditions for polymers.

The polymer molding material contains, as component B, a nitrogen-containing phosphate of the formulae $(NH_4)_yH_{3-y}PO_4$ (monophosphates) or $(NH_4PO_3)_z$ (polyphosphates), in which y may assume numerical values from 1 to 3 and z is any desired number, typically also the average value of a chain length distribution. There may be a smooth transition between the monophosphates and the polyphosphates, for example with diphosphates, triphosphates, etc. $(NH_4PO_3)_z$ typically denotes commercial ammonium polyphosphates having different chain lengths, which can be prepared by various processes. Both short-chain and long-chain polyphosphates may be used, so that z may assume, for example, values from 5 to 10,000. Poorly water-soluble,

relatively long-chain ammonium polyphosphates having chain lengths > 100 are preferred.

The amount of the phosphates (component B) to be added to the polymers may vary within wide limits. In general, from 1 to 30% by weight, based on the prepared polymer compound, are used. The optimum amount depends on the nature of the polymer, on the type of phosphinate (component A) used and on the type of the phosphate itself and can be readily determined by experiments. From 3 to 20, in particular from 5 to 15, % by weight are preferred.

Preferred thermoplastic polymers are industrial plastics, such as, for example, high impact (HI) polystyrene (having a high impact strength), polyphenylene ethers, polyamides, polyesters, polycarbonates and blends or polyblends, such as acrylonitrile-butadiene-styrene (ABS) or polycarbonate and acrylonitrile-butadiene-styrene blends (PC/ABS).

ABS polymers are particularly preferred.

The flame-retardant components A and B can be incorporated into plastics molding materials by, for example, premixing all components as powder and/or granules in a mixer and then homogenizing them in the polymer melt in a compounding apparatus (e.g. a twin-screw extruder). The melt is usually extruded, cooled and granulated. The components A and B may also be

introduced directly and separately into the compounding apparatus via a metering unit.

It is also possible to mix the flame-retardant additives A and B with prepared polymer granules or polymer powder and to process the mixture directly on an injection molding machine to give shaped articles.

In the case of polyesters, for example, the flame-retardant additives A and B may also be added to the polyester material during the polycondensation.
In addition to the flame-retardant combination according to the invention and comprising A and B, fillers and reinforcing materials, such as glass fibers, glass beads or minerals, such as chalk, may also be added to the molding materials. In addition, the molding materials may also contain other additives, such as antioxidants, light stabilizers, lubricants, colorants, nucleating agents or antistatic agents. Examples of the additives which may be used are stated in EP-A-584 567.

The flame-retardant plastics materials are suitable for the production of moldings, films, filaments and fibers, for example by injection molding, extrusion or compression molding.

Examples

1. Components used

Commercial polymers (granules):

ABS I	®Novodur P2X (from Bayer AG, D) contains no fillers or reinforcing materials
ABS II	®Novodur L3FR (from Bayer AG, D) contains bromine-containing flame-proofing composition
Polyamide 6 (PA 6)	®Durethan B29 (from Bayer AG, D) contains no fillers or reinforcing materials
Polyamide 6 (PA 6-GV)	®Durethan BKV30 (from Bayer AG, D) contains 25% of glass fibers
Polybutylene terephthalate (PBT-GV):	®Celanex 2300 GV1/30 (from Hoechst Celanese, USA) contains 30% of glass fibers

Phosphinic acid salts (component A, pulverulent):

Aluminum salt of dimethylphosphinic acid, referred to below as DMPAL

Aluminum salt of methylethylphosphinic acid, referred to below as MEPAL

Aluminum salt of 1-methoxyethylmethylphosphinic acid, referred to below as methoxy-MEPAL

Aluminum salt of methylpropylphosphinic acid, referred to below as MPPAL

Ammonium polyphosphate (component B, pulverulent):

®Hostaflam AP 422 (from Hoechst AG, D)

Antioxidants:

AO 1: ®Hostanox O 10 (from Hoechst AG, D), polynuclear phenol

AO 2: ®Hostanox PAR 24 (from Hoechst AG, D), phosphite

Light stabilizers:

LS 1: ®Hostavin N 20 (from Hoechst AG, D), sterically hindered amine, monomeric

LS 2: ®Hostavin ARO8 (from Hoechst AG, D), UV absorber, benzophenone type

The flameproofing components (phosphinic acid salts, A) and optionally the synergistic agent (ammonium polyphosphate, B) were mixed, in the ratio stated in the Tables, with the polymer granules and possibly further

additives and incorporated in a twin-screw extruder (type Leistritz LSM 30/34) at temperatures of 190-225°C (ABS) or at temperatures of 230-260°C (PA 6, PA 6-GV and PBT-GV). The homogenized polymer extrudate was taken off, cooled in a water bath and then granulated.

After sufficient drying, the molding materials were processed on an injection molding machine (type Toshiba IS 100 EN) at melt temperatures of 210-240°C (ABS) or of 240-270°C (PA 6, PA 6-GV and PBT-GV) to give test specimens, and testing for flame retardance and classification were carried out on the basis of the UL94 test (Underwriter Laboratories). The combustibility of the test specimens was rated by determining the oxygen index (LOI according to ASTM D 2863-77).

Table 1 shows the results of the comparative examples, in which phosphinic acid salts were used as the sole flameproofing components in ABS, PA 6, PA 6-GV and PBT-GV.

The results of the Examples, in which phosphinic acid salts were tested in combination with the synergistic agents according to the invention, are listed in Table 2. All stated amounts are in % by weight and are based on the prepared polymer compound including flameproofing treatment.

Table 1:

Comparative Examples. Aluminum salts of phosphinic acids as the sole flameproofing component in ABS, PA 6, PA 6-GV and PBT-GV.

Polymer	MEPAL [%]	DMPAL [%]	MPPAL [%]	Methoxy-MEPAL [%]	AO 1 [%]	AO 2 [%]	Class according to UL 94 (1.5 mm)	LOI [%]
ABS 1	30						not classifiable	52.5
ABS 1		30					V-2	51.0
ABS 1			30				V-1	38.0
ABS 1				30			V-1	46.5
PA 6	15						V-0	31.0
PA 6-GV	20						not classifiable	40.0
PBT-GV	15				0.15	0.20	V-1	48.5
PBT-GV	20				0.15	0.20	V-0	49.5

Table 2:

Examples. Aluminum salts of phosphinic acids in combination with synergistic agents according to the invention in ABS, PA 6, PA 6-GV and PBT-GV.

Polymer	MEPAL [%]	DMPAL [%]	MPPAL [%]	Methoxy-MEPAL [%]	Hosta-flam AP 422 [%]	AO 1 [%]	AO 2 [%]	Class accord-ing to UL 94 (1.5 mm)	LOI [%]
ABS 1	15				15			V-0	28.5
ABS 1	12.5				12.5			V-0	26.5
ABS 1	10				10			V-2	24.0
ABS 1	7.5				7.5			V-2	23.5
ABS 1		15			15			V-0	30.0
ABS 1			15		15			V-0	27.0
ABS 1				15	15			V-0	27.0
PA 6	10				5			V-0	n.d.*
PA 6-GV	10				5			V-0	n.d.*
PBT-GV	10				5	0.15	0.20	V-0	28.0

* n.d. = not determined

Table 3 shows the result of the exposure of a synergistic flameproofing combination according to the invention in ABS to artificial light in comparison with commercial ABS with a bromine-containing flameproofing composition in a ®Suntest apparatus from Heraeus with a Suprax filter at a black body temperature of 55°C ± 5°C without overhead aeration. The evaluation criterion is the discoloration, measured as the yellowness index (YI). In addition, the test according to UL 94 was carried out and the LOI value determined.

Table 3

Poly-mer	MEPAL [%]	Hosta-flam AP 422 [%]	LS 1 [%]	LS 2 [%]	Class acc. to UL 94 (1.6 mm)	LOI [%]	YI after 0 h	YI after 500 h	YI after 1100 h	YI after 1600 h
ABS 1			0.5	0.5	not classi-fiable	19	51	39	48	65
ABS 1	12.5	12.5	0.5	0.5	V-0	26	68	50	52	55
ABS II			0.5	0.5	V-1	25.5	29	94	101	102

The Examples reveal that a very good flameproofing effect is achieved with the combination, according to the invention, of phosphinic acid salts with synergistic agent B. In addition, the efficiency of conventional light stabilizers of the type comprising sterically hindered amines (HALS = hindered amine light stabilizer) in combination with UV absorbers is not impaired.

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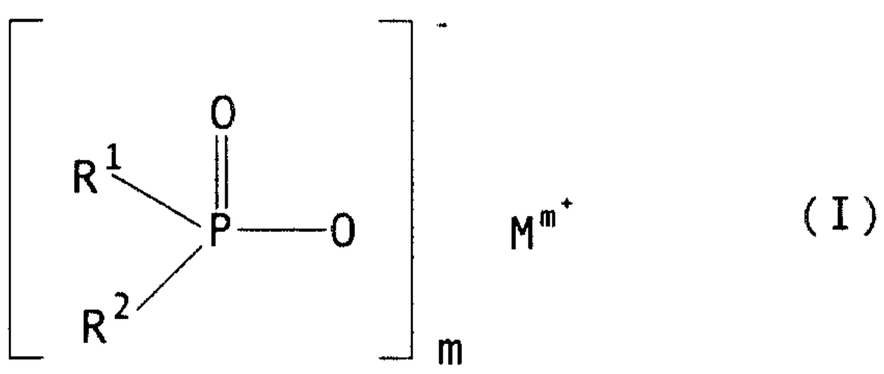
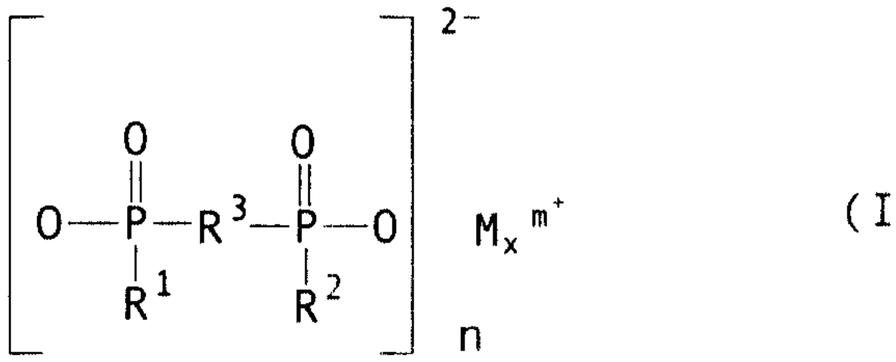
CLAIMS:

1. A synergistic flameproofing combination for polymers, containing, as component A, a phosphinic acid salt of the formula (I) and/or a diphosphinic acid salt of the formula (II) and/or polymers thereof



(I)



(II)

in which

R^1 and R^2 are linear or branched C_1-C_6-alkyl or phenyl;

R^3 is linear or branched C_1-C_{10}-alkylene, C_6-C_{10}-arylene or alkylarylene or arylalkylene,

M is a calcium, aluminum or zinc ion,

m is 2 or 3;

n is 1 or 3;

x is 1 or 2,

and, as component B, a nitrogen-containing phosphate of the formulae $(NH_4)_yH_{3-y}PO_4$ or $(NH_4PO_3)_z$, in which

y is from 1 to 3 and

z is any desired number.

2. The flameproofing combination as claimed in claim 1, wherein

R^1 and R^2 are C_1-C_4-alkyl,

R^3 is C_1-C_6-alkylene or phenylene and

M is an aluminum ion.

3. The flameproofing combination as claimed in claim 1 or 2, wherein component B comprises ammonium polyphosphates having a chain length > 100.

4. The use of a flameproofing combination as claimed in claim 1, 2, or 3 for flameproofing polymers.

5. The use according to claim 4, wherein the polymer is acrylonitrile-butadiene-styrene (ABS) polymer.

6. The use as claimed in claim 4 or 5, wherein components A and B, independently of one another, are each used in a concentration of from 1 to 30% by weight, based on the prepared polymer compound.

7. The use as claimed in claim 6, wherein components A and B, independently of one another, are each used in a concentration of from 3 to 20% by weight, based on the prepared polymer compound.

8. The use as claimed in claim 7, wherein components A and B, independently of one another, are each used in a concentration of from 5 to 15% by weight, based on the prepared polymer compound.

9. A flameproofed polymeric molding material, containing a flameproofing combination as claimed in any one of claims 1 to 3.

10. The flameproofed polymeric molding material as claimed in claim 9, wherein the polymeric molding material is an ABS polymer.

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PATENT AGENTS

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